

## **Intermediate temperature SOFC single cell test using $\text{Nd}_{1.95}\text{NiO}_{4+\delta}$ as cathode**

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### **Abstract**

This work deals with SOFC single cell tests using neodymium nickelate  $\text{Nd}_{1.95}\text{NiO}_{4+\delta}$  as cathode material. This MIEC oxide exhibits high values of both surface exchange coefficient (k) and oxygen diffusion coefficient ( $D^*$ ), as well as high electronic conductivity, which result in an enhanced electrochemical activity with respect to classical materials. The SOFC cells were fabricated from an anode supported electrolyte half cell provided by InDEC B.V. Corporation, with a 36 mm diameter. The  $\text{Nd}_{1.95}\text{NiO}_{4+\delta}$  cathode was prepared as a two stages electrode consisting of a thin interlayer of several hundred nanometers covered by a thicker layer of dozens microns. The  $\text{Nd}_{1.95}\text{NiO}_{4+\delta}$  oxide powders were synthesized using different routes in order to reduce the final annealing temperature, and to subsequently obtain submicronic powders. I-V characteristics of the single cells were investigated under hydrogen – air conditions. The power densities vs. current densities curves are reported and the results of impedance spectroscopy measurements performed under these operating conditions are discussed.

**Keywords:** Fuel Cells, mixed conducting oxides, transition metal oxides.

## 1 - Introduction

The state-of-the-art SOFC materials are based on yttria-stabilised cubic zirconia (YSZ) as electrolyte material and Ni-YSZ cermet as anode material. LSM is mostly used as cathode material despite the fact that this oxide is a poor oxygen ionic conductor. So that, high working temperature of around 1000°C is required to achieve satisfactory power density. Decreasing the temperature leads to a lower ionic conductivity of the solid electrolyte and higher polarisation resistance of the electrodes. This is particularly highlighted at the cathode side. Depending on materials, several issues are therefore explored to keep high cell performance at reduced working temperature (600-700°C). Concerning the electrolyte material, two solutions are considered: reducing its thickness or finding a new material exhibiting an ionic conductivity higher than that of the classically used yttria-stabilised zirconia. For the electrode, the cathodic overpotential may be reduced by increasing the active area for the oxygen reduction from the triple-phase-boundary (TPB) between gas, electrode and electrolyte to the whole surface of the cathode. A conceivable solution is to use mixed ionic and electronic conductors (MIEC). The  $A_2MO_4$  materials have been studied with this aim. Among those materials,  $Ln_2NiO_{4+\delta}$  have shown a wide range of oxygen overstoichiometry ( $\delta$ ). The additional oxygen atoms occupy interstitial sites in the lattice so that the structure is stabilised, and are also involved in an interstitial oxygen diffusion mechanism [1]. Moreover, in these oxides, part of  $Ni^{2+}$  cations are oxidised into  $Ni^{3+}$  cations. As a consequence, both ionic and electronic conductivities are enhanced compared to those of classical perovskite-type materials for which the ionic conduction results from a vacancy mechanism of higher activation energy [2]. The excellent electrochemical performance of the nickelates has already been demonstrated on cathode/YSZ/cathode symmetrical half cells while measuring under zero d.c. conditions [3, 4]. The present work deals with SOFC single cell tests using these cathode materials deposited onto commercial anode/YSZ half cells. Polarisation and impedance spectroscopy measurements were performed in order to quantify their performance.

## 2 – Experimental

### 2 - 1 Preparation of $Nd_{1.95}NiO_{4+\delta}$

The  $Nd_{1.95}NiO_{4+\delta}$  oxides were prepared using three different routes. The first one is based on solid state reaction. A stoichiometric mixture of rare-earth oxide ( $Nd_2O_3$ , Strem,

99.99%) and nickel oxide (NiO, Aldrich, 99.9%) was annealed at 1300°C and then thoroughly grounded using an milling attritor. After this treatment, the obtained average particle size was around 1 µm. The second route was based on a nitrate-citrate process. A stoichiometric mixture of single oxides was first dissolved in nitric acid. Citric acid was then added in a molar ratio 1:1:1. The resulting solution was heated until a self-combustion of the precipitates occurs. The final material was obtained after an annealing at 1000°C. In this case, the average particle size reached 1 µm after the attrition step. To reduce the annealing temperature and to obtain submicronic powders, a third synthesis route was therefore developed and was based on a polyacrylamide gel route [5]. Individual aqueous solutions of each cation were prepared from nitrate salts. The cations were then chelated by adding either ethylenediaminetetraacetic (H<sub>4</sub>EDTA) or triammonium citrate ((NH<sub>4</sub>)<sub>3</sub>Cit) (pH controlled via NH<sub>4</sub>OH addition). Solutions of chelated cations were mixed in a stoichiometric ratio. The organic gels were made using monomers of acrylamide to form chains and the cross-linker *N,N'*-methylene-bis-acrylamide.  $\alpha,\alpha'$ -Azobisisobutyronitrile (AIBN) dissolved in a few millilitre of acetone was used as a polymerisation initiator. The gel was transferred to a porcelain bowl and heated in a ventilated furnace at 3°C/min, up to 800°C, for 1h. A final annealing at 1000°C was required to obtain the single phase Nd<sub>1.95</sub>NiO<sub>4+δ</sub>. The average particle size was finally about 0.6 µm after an attrition stage. The polyacrylamide gel route was selected for SOFC cathode application because of the small particle size obtained by this way.

Oxide powders prepared by these three synthesis routes were characterised by X-ray diffraction using a Philips 1710 diffractometer (CuK<sub>α</sub> radiation). All samples revealed a single-phase material exhibiting the K<sub>2</sub>NiF<sub>4</sub>-type structure.

## 2 - 2 Fuel cell construction

SOFC tests were performed on single cells of anode – electrolyte – cathode systems. The samples were constructed from an anode supported electrolyte half cell produced by InDEC B.V. Corporation, having a diameter of 36 mm. The sample consists of an anode supported substrate coated with a dense 8YSZ electrolyte layer of 3 - 10 µm. The cathode was prepared as a two stages electrode consisting of a thin Nd<sub>1.95</sub>NiO<sub>4+δ</sub> interlayer of approximately 500 nm coated onto the electrolyte, covered by a thicker Nd<sub>1.95</sub>NiO<sub>4+δ</sub> layer of about 20-50 µm. The former layer was prepared by a polymeric route derived from Pechini's work [9]. The polymeric sol was dip-coated two times onto the half cell and the resulting green layer was annealed in air at 1000°C for 2 hours. A heating rate of 50°C/h was used to

prevent the formation of cracks during the thermal decomposition of organic compounds. The annealed layer was crystallized and exhibited the  $K_2NiF_4$ -type structure as shown by XRD analysis. The thick layer was prepared by the coating of a colloidal ceramic suspension made of  $Nd_{1.95}NiO_{4+\delta}$  powder dispersed in ethylene glycol. The slurry was painted onto the thin interlayer by means of a brush. The green layer was annealed in air at  $1200^\circ\text{C}$  for 20 min to ensure a strong adhesion between the two cathodic layers. The whole electrode thickness was about 20-50  $\mu\text{m}$  and the geometric area was  $3.8\text{ cm}^2$ .

## **2 – 3 I-V Characteristics**

The morphology of the powders and the microstructure of the sintered cells were characterized by scanning electron microscopy (SEM) using a JEOL JSM 6360A apparatus.

I-V characteristics of the SOFC cell assembly were investigated by monitoring the current and the terminal voltage under various loads at fixed temperature in reducing atmospheres and air. Current collectors were gold grids welded to platinum wires. The electrical contact between gold grids and electrode materials were obtained by mechanical pressure. The gastightness between the anodic and the cathodic sides was ensured by use of a glass sealant. The YSZ-NiO cermet reduction was realized at  $800^\circ\text{C}$  in agreement with InDEC standard process which consists in introducing a Ar- $H_2$  (5%) gas mixture and slowly increasing the hydrogen ratio. Electrochemical measurements were realized under the next conditions:

- Cathodic compartment: under air with a flow rate of 300mL/min or 70mL/min.
- Anodic compartment: under pure hydrogen with a flow rate of 100mL/min or 30mL/min, or under argon / hydrogen mixtures.
- Working temperatures: 800, 750, 700,  $650^\circ\text{C}$  successively.

The impedance of the cell was recorded under operating conditions using a frequency response analyzer Solartron 1260 and a potentiostat Solartron 1287.

## **3 - Results and discussion**

The cross section SEM picture of  $Nd_{1.95}NiO_{4+\delta}$  / YSZ supported SOFCs, which was fired at  $1200^\circ\text{C}$  during 20 minutes has been performed. A good adhesion between dense electrolyte and the two porous electrodes has been observed.

The open circuit voltage (OCV) of the cell was firstly measured. In agreement with the Nernst law, the OCV values were found to be in-between 1.1 and 1.2 V, depending on the working conditions. This observation allows us to conclude that both sides of the cell were efficiently sealed. Then the gas flows were fixed at 30-35 mL/min for hydrogen and 70 mL/min for air. The polarization curve obtained at 700°C is reported in Figure 1. At 800 mV, the current density is around 85mA.cm<sup>-2</sup>. By extrapolation, the current density can be estimated at about 100 to 120 mA.cm<sup>-2</sup> under 700 mV.

In order to identify the resistances associated to the polarization curve, impedance spectroscopy measurements have been performed when the cell discharged through a variable load. In these measurement conditions, it can be considered that the assembly anode/electrolyte/cathode nearly acts as a working SOFC single cell. Under open circuit conditions, impedance diagrams have been decomposed into a high frequency self part, a resistance and two capacitive loops, respectively named high frequency (HF) and low frequency (LF), associated in series. A typical impedance spectrum is shown in Figure 2. The associated electrical equivalent circuit is reported in Figure 3. The parameters values of the different impedance spectra recorded on the polarization curve are shown in Table 1. It can be seen that the first resistance series  $R_s$  is the most important resistive component. This impedance was not been clearly identified but may be attributed to an insufficient contact between the single cell and the current collectors. Indeed, the mechanical pressure applied for the set-up was lower than the value recommended by InDEC in the measurements process with anode supported cells.

The resistances  $R_{HF}$  and  $R_{LF}$  of the capacitive loops decreased versus current. This shows that these resistances are attributed to anodic and cathodic polarization resistances. Nevertheless, it is difficult to identify which semi-circle is related to the cathodic contribution. Indeed, according to previous studies [6, 8], both capacitive effects  $C \sim 0.01F$  and  $C \sim 0.3F$  associated respectively to the high frequency (HF) and the low frequency (LF) impedances, can be identified as electrode processes. Generally, the capacitive effects are more important in Triple Phase Boundaries (TPB) electrodes, such as YSZ-Ni cermet, and are lower in Internal Diffusion (ID) electrodes, as for Nd<sub>1.95</sub>NiO<sub>4+δ</sub>. One can therefore assume that the HF resistance may be attributed to the cathodic response while the LF one may rather be assigned to the anodic contribution. Results show that for low current density (high voltage), the HF resistance is the lowest contribution whereas and with further increase in current, the LF resistance forms the majority impedance. This indicates that, apart from the high resistance  $R_s$  presumably related to weak contact between the current collectors and the electrodes, the

predominant polarization resistance in the cell may be attributed to the anode. This suggests an improvement in the cell materials with respect to the usual major cathodic contribution measured on conventional SOFC cells made of TBP cathodic electrode.

The power density versus current density curves are reported in Figure 4 for 750 – 700 – 675°C. It can be noticed that for low polarization, the temperature increasing did not affect the cell performance. For current densities higher than 20mA.cm<sup>-2</sup>, the electrical properties increases and a power density of 140mA.cm<sup>-2</sup> under 700mV is obtained. At 750°C, the power density is about 90mW.cm<sup>-2</sup>.

#### **4 - Conclusion**

Accordingly, the power density demonstrates in this study on nickelate-based SOFC cell is low and unexpected with respect to the intrinsic properties of nickelates materials (high oxygen diffusion coefficient, high surface exchange coefficient and good electronic conductivity) and the good electrochemical performance already demonstrated on half asymmetrical cell. This poor performance may therefore rather be assigned to a weakness in the set up design as suggested by the high resistance  $R_s$  and to an inadequate cell shaping. These both parameters have to be further optimized to benefit from the good intrinsic properties of neodymium nickelate oxides.

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**Table**

Diagram	E (mV)	L(H)	R <sub>s</sub> (Ohm)	R <sub>HF</sub> (Ohm)	C <sub>HF</sub> (F)	R <sub>LF</sub> (Ohm)	C <sub>LF</sub> (F)
700.1	1161	2,52×10 <sup>-6</sup>	0,969	0,744	0,01246	1,070	0,3652
700.2	1121	2,53×10 <sup>-6</sup>	0,965	0,797	0,01447	1,012	0,3712
700.3	1071	2,49×10 <sup>-6</sup>	0,934	0,643	0,01260	0,825	0,4334
700.4	943	2,38×10 <sup>-6</sup>	0,872	0,543	0,01239	0,582	0,5942

Table 1 : Cell voltage and fitted values of the different parameters associated to the equivalent circuit reported in Figure 3.



## Captions

Figure 1 : Current voltage behaviour of  $\text{Nd}_{1.95}\text{NiO}_{4+\delta}$  cathode single cell operated at  $700^\circ\text{C}$  (with 30mL.min  $\text{H}_2$  and 70mL.min air).

Figure 2 : Typical complex impedance spectrum of the cell recorded at  $700^\circ\text{C}$ .

Figure 3 : Equivalent circuit used to identified the figure 2 spectrum.

Figure 4 : Power density versus current density for single cell operated at  $750^\circ\text{C}$  (●),  $700^\circ\text{C}$  (■) and  $675^\circ\text{C}$  (▲)

**Figures :**

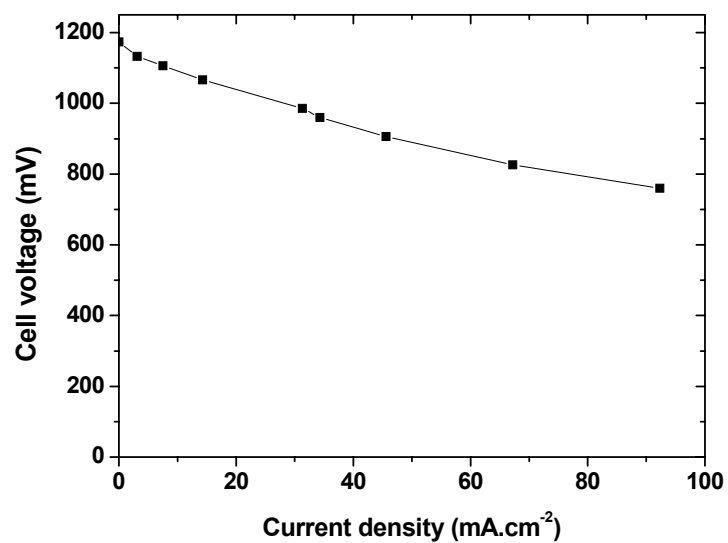


Figure 1 : Current voltage behaviour of  $\text{Nd}_{1.95}\text{NiO}_{4+\delta}$  cathode single cell operated at  $700^\circ\text{C}$  (with  $30\text{mL.min}^{-1}$   $\text{H}_2$  and  $70\text{mL.min}^{-1}$  air).

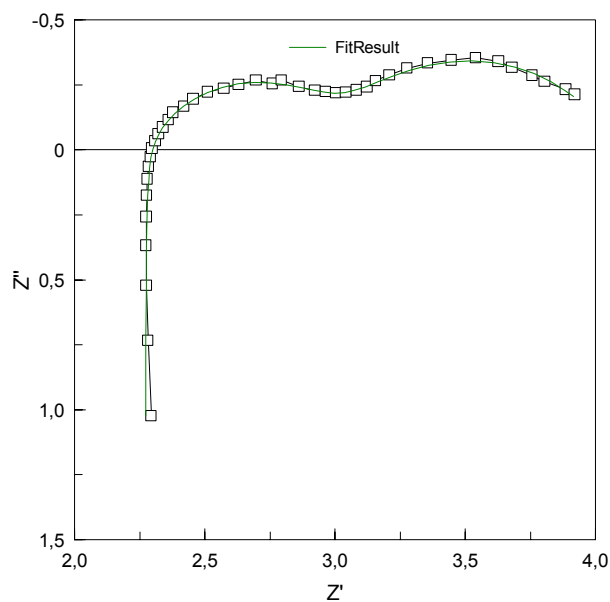


Figure 2 : Typical complex impedance spectrum of the cell recorded at  $700^\circ\text{C}$  under open circuit conditions.

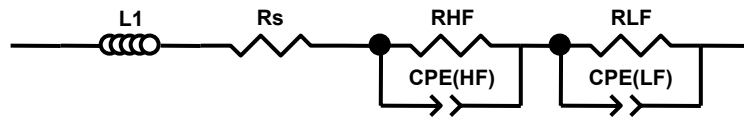


Figure 3 : Equivalent circuit used to identified the figure 2 spectrum.

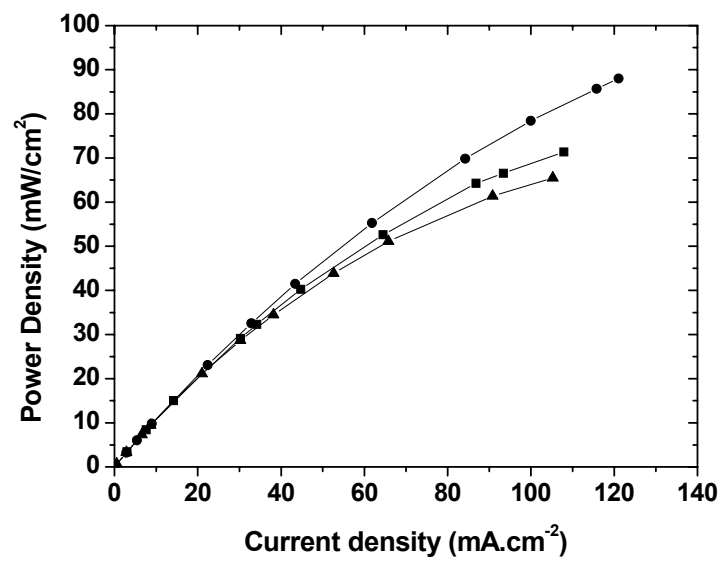


Figure 4 : Power density versus current density for single cell operated at 750°C (●), 700°C (■) and 675°C (▲)